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(54) Title: IMPROVED ALUMINA-SUPPORTED COPPER CATALYST COMPOSITIONS FOR FLUID-BED HYDROCARBON OXYHYDROCHLORINATION

(57) Abstract

A catalyst composition is provided having copper chloride deposited on a fluidizable alumina support in which the support has incorporated prior to deposit of copper from 0.5 to 3.0% by weight of at least one alkali metal, alkaline earth metal or rare earth metal. Such catalyst composition is used as the fluid bed catalyst in the vapor phase reaction of ethylene, oxygen and hydrogen chloride to produce 1,2-dichloro-ethane. This results in improved yield and efficiency of EDC production based on ethylene and avoids operating problems caused by stickiness in the fluid bed. Incorporation of a combination of potassium and barium in the fluidizable alumina support prior to deposit of copper produces an excellent catalyst for the fluid bed ethylene oxyhydrochlorination process in which the vent gases are recycled.

IMPROVED ALUMINA-SUPPORTED COPPER CATALYST COMPOSITIONS FOR FLUID-BED HYDROCARBON OXYHYDROCHLORINATION

BACKGROUND OF THE INVENTION

This invention pertains to fluid bed catalytic oxyhydrochlorination of hydrocarbons, particularly ethylene, to produce chlorinated hydrocarbons, particularly 1,2 dichloroethane, commonly called ethylene dichloride (EDC) and relates specifically to improved alumina-supported copper catalysts and their use in such oxyhydrochlorination.

The production of chlorinated hydrocarbons by oxyhydrochlorination (sometimes called more simply "oxychlorination") of hydrocarbons containing 1 to 4 carbon atoms is well known to the art. A particularly advantageous process for oxyhydrochlorination of ethylene to produce EDC, practiced in many highly successful commercial installations throughout the world, involves the reactions in the vapor phase over a fluidized catalyst bed, of a mixture of ethylene, hydrogen chloride (HCl) and oxygen, or an oxygen containing gas (e.g., air), in the manner and under the conditions generally described in Harpring et al U.S. Patent 3,488,398. In commercial operation of this process the molar ratio of ethylene to oxygen to HCl is maintained in the range of about 1.0 to 1.2 moles ethylene to about 0.55 to 0.9 moles oxygen for each 2 moles of HCl; the temperature is maintained in the range of 200 to 250°C. and the pressure is normally in the range of 10 to 50 psi.

The fluidized catalyst bed heretofore used in commercial operation consists of about 2 to 10% by weight of a copper compound, preferably copper chloride, as the active catalytic ingredient, uniformly deposited on fine particles of a fluidizable alumina support. The alumina support material, which is preferably gamma alumina but can also be "Condea" alumina, on the so-called microgel alumina or other forms of "activated" alumina, resembling

fine sand, is of such a nature as to be readily fluidizable without excessive catalyst loss from the reaction zone, by virtue of having the proper bulk density, resistance to attrition and a preselected ratio of particle sizes and also, in order to provide ample reaction sites of copper catalyst, has a surface area, after copper is deposited thereon, in the range of 60 to 160 square meters per gram (m^2g).

However, the supported catalyst functioning in the fluid bed oxyhydrochlorination of ethylene, as above described, could desirably be improved in two significant respects.

First, it would be desirable for the catalyst to effect a higher than normal EDC efficiency based on ethylene (i.e., for the ethylene reactant to be more completely converted to EDC with less being converted to carbon oxides - carbon monoxide and carbon dioxide). This is especially desirable when the ethylene oxyhydrochlorination process as described in the Harpring et al patent (which in its exemplified embodiments used air to supply oxygen) is adapted to recycle the gases normally vented to the atmosphere, in order to avoid releasing hydrocarbons and chlorinated hydrocarbons to the environment, with introduction of essentially pure oxygen rather than air with the recycle stream. This variation of the ethylene oxyhydrochlorination process is termed herein, for brevity, "oxyvent reçycle" and is described in more detail in Anoto et al U.S. Patent 4,071,572 and especially in Hoechst A.G. Belgian Patent 866,157.

Secondly, the copper-on alumina fluidized catalyst exhibits during the oxyhydrochlorination reaction a pronounced tendency to develop "stickiness" and cause severe disruption of process operations. This problem and means for its partial control are described in the copending application of Joseph Allen Cowfer, Dane Edward Jablonski, Ronald Michael Kovacs and

Angelo Joseph Magistro S.N. 949,170 filed November 6, 1978 and a method and composition for alleviating or eliminating stickiness in the catalyst through use of bare alumina support and deposition of copper on bare support in situ are described in the copending related application of Joseph Alan Cowfer, Jamal Shahab Eden and Angelo Joseph Magistro filed concurrently herewith.

Finally, by way of background, it has been proposed in numerous prior art patents to conduct hydrocarbon oxychlorination reations in a fluid bed in which the fluidized catalyst consists of a mixture of copper chloride with other metal chlorides especially potassium chloride (instead of using copper alone) both deposited on a fluidizable support. For example, U.S. Patent 3,427,359 describes a catalyst composition for fluid-bed oxychlorination of hydrocarbons and partially chlorinated hydrocarbons, such as methane and methylene chloride, consisting of copper chloride, an alkali metal chloride and a rare earth metal chloride supported on an inert carrier material such as alpha alumina having a surface area no greater than 10 m^2g. However, the expedient of depositing one or more other metals with copper on the alumina support described above, and using such a supported catalyst in the fluid bed ethylene oxychlorination process described above, does not materially inprove ethylene efficiency to EDC and, moreover, results in significantly increased stickiness of particles in the fluid bed. Consequently, this prior art does not point to the improvement desired in either of the two aspects noted hereinabove.

SUMMARY OF THE INVENTION

It has now been discovered, unexpectedly, that the incorporation of certain specified metals in certain proportions into the alumina support material conventionally used in preparation of the hereinabove described alumina supported copper catalysts for fluid bed

ethylene oxyhydrochlorination to produce EDC, prior to and independently of depositing copper catalyst on the support, results in a novel improved alumina-supported copper catalyst which when used as the fluid bed in the oxyhydrochlorination of ethylene to EDC enables attainment of significantly improved efficiency of EDC production based on ethylene and further exhibits improved fluidization properties, not developing stickiness in use to the extent of a similar catalyst bed in which the alumina support material has not been modified by having a metal as specified incorporated therein.

The metal so incorporated may be an alkali metal, an alkaline earth metal, a rare earth metal or a mixture of one or more such metals as will be described. The incorporation of a mixture of an alkali metal and an alkaline earth metal into gamma alumina support, after which copper is deposited thereon, produces a supported catalyst particularly effective for oxyvent recycle oxyhydrochlorination of ethylene.

Incorporation of the specified metal or metals into the alumina support is accomplished conveniently by inpregnating the support with an aqueous solution of a water soluble salt of the metal or metals in question, drying the wetted support and then calcining at elevated temperatures for several hours to produce an intimate admixture of the finely divided fluidizable alumina with the finely divided metal or metals in question probably in the form of complex oxides, and having essentially the same physical characteristics as the fluidizable alumina before metal is incorporated therein. The proportion of added metal in the so-modified alumina support is in the range of 0.5 to about 3.0% by weight.

Deposit of copper preferably as copper chloride, on the alumina support modified by incorporation of metal as described, produces the novel fluidizable catalyst composition of this invention. Deposit of copper on the

modified support is effected in any known manner either entirely before the catalyst composition is placed in an oxyhydrochlorination reactor to function as the fluid bed or at least partly in situ in the manner described in the aforementioned concurrently-filed application of Cowfer, Eden, and Magistro.

When the novel catalyst composition is used as the fluid bed in the process of oxyhydrochlorination of ethylene to EDC under normal reaction conditions, conversion of ethylene are generally above 98%, and 98% or more of the ethylene converted yields EDC (i.e., a maximum of only about 2% of the ethylene converted leaks to carbon oxide formation) so that the EDC efficiency based on ethylene (% conversion of ethylene x % yield EDC based on ethylene) is of the order of 97% or higher. This efficiency compares with an EDC efficiency based on ethylene generally in the order of 90%, and at best no more than 93 - 94%, when using the conventional catalyst composition - copper supported on alumina without prior incorporation of metal with the alumina. Further, the incorporation of metal in the alumina support renders the catalyst composition less "stickiness-prone" during the course of the oxyhydrochlorination reaction. Accordingly, this invention provides, in addition to a novel and improved catalyst composition, an improved fluid-bed hydrocarbon oxyhydrochlorination process characterized in that the fluid bed is composed of the novel catalyst composition.

DETAILED DESCRIPTION OF THE INVENTION

The alumina support material used in preparing the modified alumina support material on which copper is deposited to form the catalyst compositions of this invention is readily available to catalyst manufacturers and is not strictly critical so long as it is of such characteristic as to be readily fluidizable. As previously mentioned, various types of finely divided

fluidizable aluminas may be used, the material known as "gamma alumina" being especially suitable. The alumina material used normally has a surface area in the range of 60 to 200 m^2g, a bulk density in the range of 0.9 to 1.1 grams per c.c., a pore volume in the range of 0.2 to 0.5 c.c. per gram and a particle size distribution such that about 75 to 92 weight percent of the particles are below 80 microns in diameter, about 40 to 50 percent below 45 microns in diameter and about 15 to 30 percent below 30 microns in diameter with no more than 1 to 5% larger than 200 microns or more than 3 to 10% below 20 microns. Such alumina materials are relatively stable, mechanically strong and resistant to attrition so that excessive quantities are not lost from the fluid bed reaction zone when used as catalyst support in fluid bed reactions.

It is recognized that some conventional alumina support materials may inherently contain in addition to Al_2O_3 traces of other metal oxides such as sodium oxide. It is understood that use of such supports without modification through incorporation of added amounts of the metals herein specified forms no part of this invention.

The modified alumina support material used in this invention is prepared by first wetting an unmodified, conventional alumina support, as above described, with an aqueous solution of a salt of the required metal or metals; the so-wetted alumina then dried to remove water and then calcined for 5810 hours at an elevated temperature in the range of 300 to 600°C. during which the added metal salt is converted to metal oxide. An amount of metal salt is chosen so that the final modified alumina support contains from 0.5 to 3.0% by weight of incorporated metal.

The metal salt in the aqueous solution can be any desired soluble salt, such as a chloride, carbonate,

of an alkali metal such as potassium, lithium, sodium, rubidium or cesium, preferably potassium or lithium, or of an alkaline earth metal such as calcium, strontium or barium, preferably the latter, or of a rare earth metal such as lanthanum or cerium or a mixture of rare earth metals such as the mixture called didymium which contains lanthanum and neodymium together with smaller amounts of praesodymium and samarium and even smaller amounts of other rare earth metals. Other mixtures of salts of the same or different metals recited, wether or not of the same class, may also be used; a mixture of a salt of an alkali metal, particularly potassium, with a salt of an alkaline earth metal, particularly barium, is especially desirable.

The modified alumina support having 0.5 to 3.0% of metal incorporated therein, prepared as above described, possesses physical characteristics as described for the conventional unmodified alumina support and can have copper catalyst, such as cuprous chloride or other cuprous or cupric salt, deposited thereon by the same techniques as used in formation of the known alumina-supported copper catalysts. The amount of copper deposited will depend on the activity desired and the specific fluidization characteristics of the support and can be as little as 2% by weight or as much as 10 to 12% by weight of the modified support material. The final catalyst composition containing the copper catalyst on the modified support is fluidizable like the support but certain specific characteristics, surface area and pore volume, for example, are, of course, modified by reason of the deposit of copper. The preferred catalyst compositions of this invention have a surface area in the range of 50 to 160 M^2g, some 15-20% lower than that of the support before deposit of copper.

The specific Examples set forth below further illustrate the nature of the catalyst composition of this

invention, and especially their use to improve the fluid bed process for oxyhydrochlorination of ethylene to produce EDC. In each Example the catalyst composition is prepared using gamma alumina of the characteristics specified to prepare the modified support on which $CuCl_2$ is deposited and the fluid bed ethylene oxyhydrochlorination to form EDC is conducted in a bench scale fluid bed reactor of 22 mm. internal diameter and 24 inches heighth charged with 125 ml. of the fluid bed catalyst composition as described. The reactor is equipped with means for delivering the gaseous reactants - ethylene, oxygen (as air) and HCl - through the fluid bed reactor zone, for controlling the quantities of reactants and reaction conditions and for ascertaining from the effluent gases the conversion and yield of ethylene to EDC and carbon oxides.

EXAMPLE I

This Example illustrates the preparation and use in ethylene oxyhydrochlorination to EDC of catalyst compositions consisting of copper deposited on fluidized alumina support modified by incorporation of an alkali metal.

Four catalyst compositions are prepared as follows: (A) gamma alumina is impregnated with 1% aqueous K_2CO_3 dried in a steam bath and calcined for 8 - 10 hours at 400°C. after which the K-modified alumina support is impregnated with 10% cupric chloride, dried slowly, calcined 8 - 10 hours at 275°C. and sieved to 80 - 325 mesh; (B) same as (A) except calcined after addition of K_2CO_3 and drying at 570°C.; (C) same as (A) except LiCl used in place of K_2CO_3 and (D) same as (A) except CsCl used in place of K_2CO_3.

Each catalyst composition is then separately charged to the fluid bed reactor where ethylene, oxygen and HCl in the molar ratios of 1.0 to 0.8 to 2.0 are reacted to form EDC under the conditions and with the yields and efficiencies as shown in Table I.

TABLE I

Catalyst	Reaction Temp. °C.	Reactants Contact Time Seconds	% Conv. C_2H_4	% Yield			% Efficiency EDC
				CO	CO_2	EDC	
A	220	13.1	98.1	0.21	0.58	99.0	97.1
	226	12.9	99.1	0.60	0.95	98.1	97.2
	220	14.4	98.6	0.62	0.82	98.4	97.0
	225	14.2	99.5	0.54	0.95	98.2	97.8
	221	16	99.5	0.59	1.03	98.1	97.6
	225	17.5	99.7	0.27	0.70	98.6	98.2
	220	21.1	100	0.59	1.21	97.9	97.9
B	221	10.4	97.4	0.27	0.42	99.1	96.7
	221	11.5	98.2	0.33	0.69	98.8	97.0
	225	11.4	98.2	0.26	0.54	98.9	97.1
	230	11.3	98.7	0.17	0.33	99.2	97.9
	235	11.2	100	0.59	0.83	98.0	98.0
C	220	11.0	98.6	0.15	1.19	98.3	97.0
	225	10.9	99.7	0.32	1.33	97.9	97.5
	220	13.2	99.5	0.18	1.37	98.1	97.6
	225	13.1	100	0.73	1.55	97.2	97.2
	220	15.8	99.7	0.71	1.42	97.4	97.2

TABLE I (cont.)

Catalyst	Reaction Temp. °C.	Reactants Contact Time Seconds	% Conv. C_2H_4	% Yield CO	% Yield CO_2	% Yield EDC	% Efficiency EDC
D	220	12.7	98.8	0.5	1.03	98.3	96.8
	220	15.8	100	0.76	1.41	97.5	97.5
	220	20.0	100	0.81	2.07	96.6	96.6

It is noted from Table I that the EDC efficiency based on ethylene with each catalyst composition and under each reaction condition, is of the order of 97 - 98%. When, however, the same catalyst composition except for being prepared from the unmodified alumina support without first incorporating the alkali-metal therein is used in a "control" under the same reaction conditions, the maximum EDC efficiency based on ethylene is only of the order of 93 - 94%. Further, the fluid bed catalyst compositions used do not develop "stickiness" in use as occurs in another "control" when the alkali metal salt is deposited on the alumina support with the cuprous chloride catalyst.

EXAMPLE II

This Example illustrates catalyst compositions, and their use in fluid bed oxyhydrochlorination of ethylene to EDC, in which an alkaline earth metal is incorporated in the alumina support prior to deposit of $CuCl_2$ thereon. The catalyst composition is made by the procedure of Example I with the same materials except that 1% $Ba(OH)_2$ is used to prepare the modified support and the calcination temperature in its preparation is 570°C. This catalyst composition is used in the fluid bed oxyhydrochlorination of ethylene to EDC as described in Example I with a reaction temperature of 225°C. and a contact time of 10 seconds for a period of 14 - 18.5 hours. The ethylene conversions, EDC yield and EDC efficiency based on ethylene is shown in the following data:

Elapsed Time Hours	% Conversion C_2H_4	% EDC	
		Yield	Efficiency
14	98.9	97.7	96.6
15.5	99.0	98.2	97.2
17.5	99.0	98.3	97.3
18.5	99.1	97.5	96.6

EXAMPLE III

This Example illustrates catalyst compositions prepared using rare earth metals and their use in ethylene oxyhydrochlorination. Catalyst compositions are prepared as in Example I but using lanthanum chloride ($LaCl_3$) and chlorides of rare earth metal mixture (RE Cl_3) respectively. They are used as in Example I in fluid bed oxyhydrochlorination of ethylene and reaction temperatures of 217°C. and 218°C., respectively; contact times of 11 and 17 seconds, respectively and molar ratios of C_2H_4 to O_2 to HCl of 1.0/.8/2.13 and 1.0/.8/2.02, respectively, with the following results:

Metal Salt	% Conversion C_2H_2	% EDC	
		Yield	Efficiency
La Cl_3	99.3	98.3	97.6
RE Cl_3	99.8	97.2	97.0

EXAMPLE IV

A catalyst composition is prepared and used as in Example I except that a mixture of 1% KCl and 1% $BaCl_2$ is used to prepare the modified support on which $CuCl_2$ is deposited; the ratio of C_2H_4 to O_2 to HCl is 1/1.8/2.1 and the reaction is continued for a total of 282 hours. The data obtained are shown in Table II.

TABLE II

Reaction Temp. °C.	Contact Time Seconds	Elapsed Time Hours	% Conversion C_2H_4	% EDC Yield	% EDC Efficiency
225	10.5	6	98.2	99.8	98.3
225	10.5	27	98.3	99.4	97.8
220	12.7	48	100	99.2	99.2
218	12.7	168	98.7	99.0	97.7
218	11.1	222	96.6	99.6	96.3
220	11.0	233	96.9	99.1	96.1
215	13.7	236	96.8	99.6	96.4
220	13.6	279	98.5	99.2	97.7
218	17.3	282	99.3	99.0	98.4

Table II shows, in comparison to Table I, that yield of EDC from ethylene converted is above 99% even when the ratio of HCl in the reactants is increased and that efficiency of EDC is at 97 - 98% over a period of several days. This indicates that the catalyst composition of this Example is an excellent fluid bed catalyst for ethylene oxyhydrochlorination conducted with oxygen recycle since the relative proportion of carbon oxides in the vent gas to be recycled is reduced and excess HCl in the feed does not reduce EDC efficiency based on ethylene.

Although the Examples presented above all illustrate the use of the catalyst compositions of this invention in the fluid bed oxyhydrochlorination of ethylene to EDC and the advantages thereby achieved, it is to be understood that such catalyst compositions are also effective in the fluid bed oxyhydrochlorination of other gaseous hydrocarbons containing 1 to 4 carbon atoms such as methane, ethane, propylenes, propane, butylenes, butanes, etc. to produce other chlorinated hydrocarbons. They can be used advantageously wherever it is desired to have copper catalyst available on a fluidizable support.

CLAIMS

1. A catalyst composition comprising a copper catalyst deposited on a fluidizable alumina support in which is incorporated, prior to deposit of the copper catalyst, from 0.5 to 3.0% by weight of at least one added metal selected from the class consisting of alkali-metals, alkaline earth metals and rare earth metals.

2. The composition of Claim 1 wherein the fluidizable alumina support is gamma alumina.

3. The composition of Claim 1 wherein the metal incorporated in the alumina support is an alkali metal.

4. The composition of Claim 1 wherein the metal incorporated in the alumina support is an alkaline earth metal.

5. The composition of Claim 1 wherein the metal incorporated in the alumina support is a rare earth metal.

6. The composition of Claim 2 wherein the metal incorporated in the alumina support is potassium.

7. The composition of Claim 2 wherein potassium and barium are incorporated in the alumina support.

8. In the process of oxyhydrochlorinating ethylene to produce 1,2-dichloroethane by contacting a vaporous mixture of ethylene, oxygen and hydrogen chloride with a fluidized catalyst composition disposed in a reaction zone and recovering 1,2-dichloroethane from the effluents of the reaction zone, the improvement in which the fluidized catalyst composition consists of 2 to 12% copper chloride supported on a fluidizable alumina in which is incorporated, prior to deposit of copper thereon, from 0.5 to 3% by weight of at least one added metal, said metal being selected from the class consisting of alkali metals, alkalene earth metals and rare earth metals.

9. The process of Claim 8 further characterized in that the added metal is potassium.

10. The process of Claim 8 further characterized in that the fluidizable alumina support has incorporated therein, as added metals, both potassium and barium.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 80/01375

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INC. CL.3 C07C 17/02, B01J, 27/06, C01B 7/00
US. CL. 570/243, 245 252/441, 443, 423/502

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	570/243, 245 252/441, 442 423/502

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A, 3,488,398, Published, 06 January 1970, Harpring, et al.	1-10
A	US, A, 2,271,056, Published, 27 January 1942, Balcar	1-10
A	US, A, 3,461,181, Published, 12, August 1969 Sato	1-10
A	US, A, 4,124,534, Published, 07 November 1978, Leitert	1-10
A	US, A, 3,427,359, Published, 11 February 1969, Rectenwald	1-10
A,P	US, A, 4,206,180, Published, 03 June 1980 Campbell	1-10
A	US, A, 4,069,170, Published, 17 January 1978, Blake	1-10
A	US, A, 3,642,921, Published, 15 February 1972, McCarthy	1-10

* Special categories of cited documents: [15]

"A" document defining the general state of the art
"E" earlier document but published on or after the international filing date
"L" document cited for special reason other than those referred to in the other categories
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but on or after the priority date claimed
"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention
"X" document of particular relevance

IV. CERTIFICATI N

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
05 FEBRUARY 1981	19 FEB 1981
International Searching Authority [1]	**Signature of Authorized Officer [10]** D. E. Gantz
ISA/US	J.A. BOSKA DELBERT E. GANTZ SUPERV. PRIMARY EXAMINER

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FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 3,709,950, Published, 09 January 1973 Baker, et al.	1-10
A	CA. A , 695,895, Published, 13 October 1964, Millidge, et al.	1-10
A	CA. A , 701,913, Published, 12 January 1965, Capp, et al.	1-10

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers ______, because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers ______, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.